High T_c thin films with roughness smaller than one unit cell

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We have developed a method for the growth of epitaxial high T_c superconducting thin films with roughness smaller than one unit cell using conventional magnetron sputtering. In this method the substrate is positioned above one edge of the target (off axis) to avoid resputtering, and oscillated back and forth between the two symmetrical edges of the target to improve film thickness homogeneity. Finite size peaks in the x-ray diffraction spectra of thin $GdBa_2Cu_3O_{7-\delta}$ films and satellite peaks on a $GdBa_2Cu_3O_{7-\delta}/YBa_2Cu_3O_{7-\delta}$ superlattice show the excellent thickness control and smoothness obtained with this technique.

Sputtering is a desirable technique for the preparation of high T_c thin films although *in situ* growth is complicated by resputtering effects.[1,2] In order to obtain stoichiometric films by single target sputtering, mainly two approaches have been used. In the first, [Fig. 1(a)] "on-axis" geometry (substrate surface facing the target surface and substrate above the target) is used and the resputtering is compensated by tuning a generally narrow window of optimal parameters for deposition. Compensated composition (not 1:2:3) targets are usually used in this method although some reports have claimed the use of stoichiometric targets.[3,4] The second [Fig. 1(b)], "off-axis" geometry (substrate surface perpendicular to the target surface and substrate outside glow discharge area) is used to avoid resputtering effect.[5,6] This method seems to give good, reproducible results relatively easily. However there are disadvantages in off-axis sputtering. Commonly it requires sputtering guns specifically designed for high T_c films, special geometries if multilayers are grown, and the film thickness is often inhomogeneous.

In this letter, we present the growth of high-quality high T_c thin films with excellent thickness homogeneity using a sputtering system of conventional geometry with planar magnetron sources and with parallel target and substrate surfaces. In this system (Microscience Researcher 101) several planar dc magnetron sputtering guns (Ion Tech model 314C) using 38-mm-diam targets are aimed vertically. The substrate holder is attached to a stepping motor driven axle which moves in a circumference above all sputtering sources. The sintered oxide targets are prepared from better than 99.9% pure R_2O_3, $BaCO_3$, and CuO. The mixed powders are calcined in air at $\approx$900 °C for 3 h, ground in a ball mill, pressed into the proper shape and sintered in air at $\approx$930 °C for 3 h. Typical densities are of the order of 60%. The cation composition of the targets is chosen in between 1:2:3 and 1:2.05:3.10 determined by film composition analysis using energy-dispersive x-ray analysis (EDX). The structure of the films is studied by CuK_α x-ray diffraction (XRD) and the resistivity and superconducting critical temperature are measured with standard four probe dc technique.

Figure 1(c) shows schematically the 0° off-axis technique[7] which combines the advantages of the on-axis and off-axis techniques. The substrate and target surfaces are kept parallel which permits the deposition of 1:2:3 and standard materials in the same chamber. The substrate is kept outside the glow discharge area, which avoids resputtering effects. In this geometry the *composition* of a film grown on a 10×10 mm substrate is homogeneous within 10%. However, the film *thickness* is a factor of 2 different at the two edges of the substrate as measured by contact profilometry. This problem is solved in the not aligned, chopped power, oscillatory (NACHOS) technique presented here [Fig. 1(d)] by periodically moving the substrate between the two edges of the target. During the time the substrate spends over the target the discharge power is reduced by a factor of 10 to prevent off-stoichiometric film deposition due to resputtering while keeping the plasma ignited.

Typical deposition conditions are as follows: vertical distance between target and substrate surface $\approx$30 mm; horizontal distance between target center and substrate

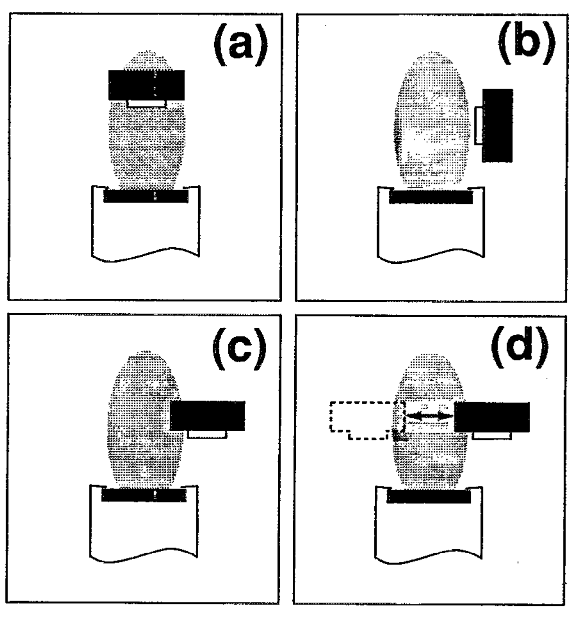

FIG. 1. Schematics of the (a) on axis. (b) 90° off-axis, (c) 0° off-axis, and (d) NACHOS deposition geometries showing the relative positions of target, substrate, and glow-discharge area.

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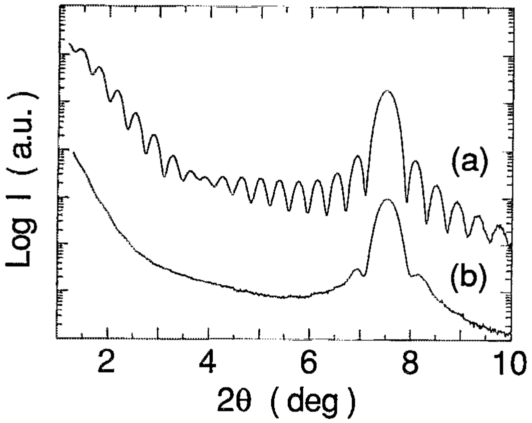

FIG. 2. Low-angle x-ray diffraction spectra of (a) 232 Å $GdBa_2Cu_3O_{7-\delta}$ thin film grown on (100)$SrTiO_3$ by the NACHOS method and (b) thin film grown at the same deposition time and conditions as film (a) by the 0° off-axis method.

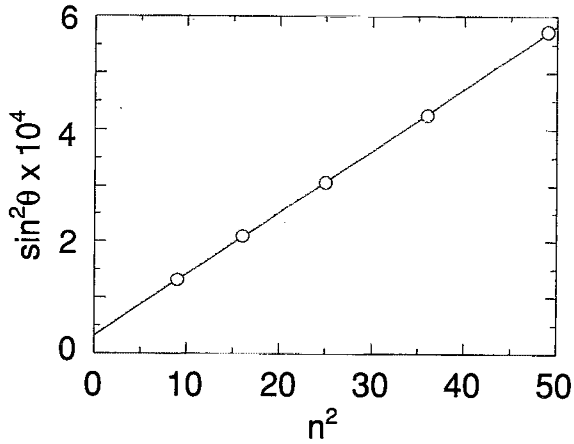

FIG. 4. $\sin^2\theta$-vs-n^2 plot for the minima below 3° in Fig. 2(a). Solid line is the least-squares linear fit to the data. The film thickness is calculated from this slope (see text for details).

center ≈30 mm (for a target diameter of 38 mm); substrate temperature 700–800 °C; sputtering gas 10% O_2/90% Ar at a pressure of 300 mTorr, dc sputtering power of 25 W.[8] With these parameters, the deposition rate is typically 0.2–0.3 Å/s. The time spent on each side of the substrate is dependent on the desired film thickness and varied between 5 s and 5 min while the crossing time over the target is ≈1s. After deposition the chamber is filled with 100 Torr of pure oxygen and the substrate is cooled down to room temperature in about 2 h. The optically polished (100)$SrTiO_3$ substrates are cleaned ultrasonically in organic solvents (trichloroethylene, acetone, and methanol) without any additional surface treatment and are bonded on the heater block with indium.

Figures 2 and 3 show the low- and high-angle θ-2θ XRD spectra of a NACHOS ≈200 Å $GdBa_2Cu_3O_{7-\delta}$ film. For comparison Fig. 2 includes the low angle θ-2θ spectra for a 0° off-axis film with the same total deposition time and conditions. The difference between both spectra is quite remarkable. While the 0° off-axis film shows only the (00n) Bragg peaks from the crystalline structure, the NACHOS film also shows clear finite size peaks. The fact the eight orders of finite size peaks are clearly seen around each Bragg peak indicates that the thickness of the film cannot fluctuate more than $1/8 = 12.5\% \approx 2$ unit cells. This gives an upper limit for the thickness fluctuations needed to smear completely the finite size peaks. The sharpness of the peaks together with their number imply that the film is flat to within one unit cell in distances of the order of the x-ray coherence length, which is typically several hundred Ångstroms. The rocking curve of the (005) reflection has a full width at half-maximum of 0.08° indicating also high crystalline orientation. However the c-axis lattice constant calculated from the Bragg peak positions is 11.78 Å, which is larger than the typical value of 11.72 Å found in thicker (≈2000 Å) films. This suggests the film is in a strained state.

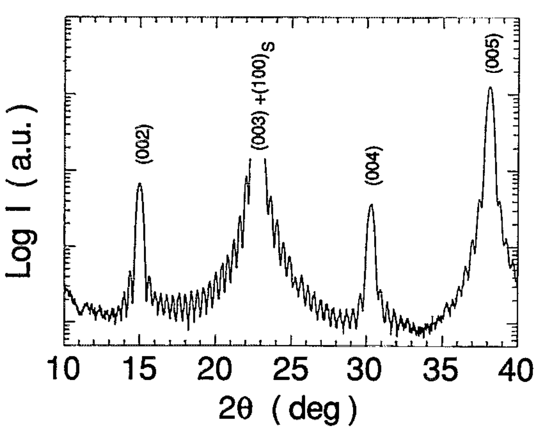

FIG. 3. High-angle x-ray diffraction spectra and the same film shown in Fig. 2(a). Indexing is for $GdBa_2Cu_3O_{7-\delta}$ peaks; $(100)_s$ labels the (100)$SrTiO_3$ diffraction peak.

The observation of finite size peaks allows an accurate measurement of the film thickness. After taking into account the effects due to the index of refraction of the film the 2θ values for the low-angle minima and maxima are given by[9]

$$\sin^2\theta = [(n+k)\lambda/2d]^2 + 2\delta, \tag{1}$$

where d is the thickness of the film, λ is the x-ray wavelength, $1-\delta$ is the real part of the index of refraction of the film, $k=0$ for an intensity minimum, and $k=1/2$ for an intensity maximum if the substrate has a lower electron density than the film. Figure 4 shows the $\sin^2\theta$-vs-n^2 plot for the low-angle minima below 3° in Fig. 2. The slope of the linear fit gives $d=232$ Å and the intercept $2\delta = 3.2\times10^{-5}$, in agreement with the expected value of 3.7×10^{-5}.[9] We routinely use this method to determine the thickness of the films and thus the deposition rate. As a cross check we can also roughly estimate the thickness of the film through Scherrer's formula[10]

$$d = 0.9\lambda/(B\cos\theta_B), \tag{2}$$

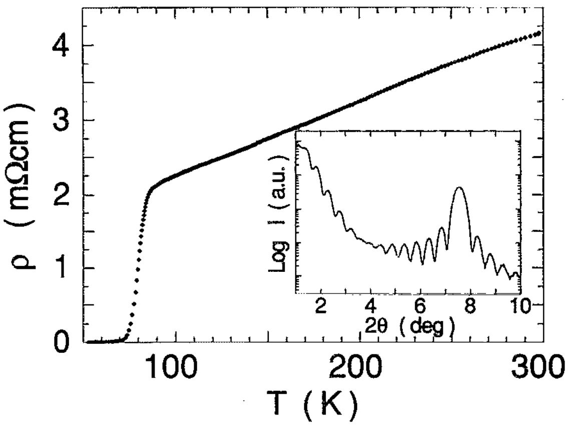

FIG. 5. Resistivity-vs-temperature curve for a 181-Å – thick NACHOS $GdBa_2Cu_3O_{7-\delta}$ film on (100)SrTiO$_3$. Inset shows the low-angle x-ray diffraction spectra of this film.

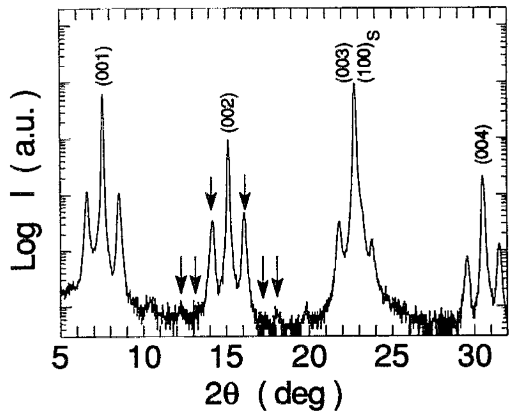

FIG. 6. X-ray diffraction spectra for a $GdBa_2Cu_3O_{7-\delta}$ (4 unit cells)/$YBa_2Cu_3O_{7-\delta}$ (4 unit cells)×21 superlattice grown on (100)$SrTiO_3$. The arrows show the first to third order superlattice satellite peak positions around the (002) reflection. The full width at half-maximum of the rocking curve of the (007) reflection is 0.23°.

where B is the full width at half-maximum of the Bragg peak located at θ_B. Using $B=0.36°$ for the (001) peak at $2\theta=7.5°$, Eq. (2) gives $d=223$ Å in good agreement with the result of Eq. (1), especially since neglecting instrumental broadening we give a lower estimate for the thickness. Direct measurement using contact profilometer on thicker films shows thickness homogeneity within ±10% in the whole deposition area (20×10 mm). The resistivity versus temperature for a 181 Å NACHOS film (Fig. 5) has a midpoint transition temperature of 80 K and a 10%–90% transition width of 7 K. One possible explanation for this suppressed T_c and high resistivity is the strained state of the film described earlier.

The excellent thickness controllability obtained with this method is also proven by the XRD spectra (Fig. 6) of a c-oriented $GdBa_2Cu_3O_{7-\delta}$ (4 unit cells)/$YBa_2Cu_3O_{7-\delta}$(4 unit cells) superlattice with total thickness of ≈2000 Å. The superlattice modulation length Λ obtained from the refinement of the spectra[11] is 92.8 Å, within 1% of the intended value of 8 unit cells, 93.6 Å with a suppression of the second order satellite peaks due to the equal thicknesses of the $GdBa_2Cu_3O_{7-\delta}$ and $YBa_2Cu_3O_{7-\delta}$ layers. This film has $T_c=91.0$ K and $\Delta T_c=1.4$ K with resistivity ratio $\rho(300\ \mathrm{K})/\rho 100\ \mathrm{K})=3.0$.

In conclusion, we have grown high-quality, smooth high-T_c thin films using a modification of the conventional sputtering geometry. In this NACHOS method the flatness of the films is improved by oscillating the substrate so as to compensate for thickness inhomogeneities. The XRD finite size peaks on thin $GdBa_2Cu_3O_{7-\delta}$ films show that the roughness of the film is less than or comparable to one unit cell. X-ray diffraction spectra for $GdBa_2Cu_3O_{7-\delta}$/$YBa_2Cu_3O_{7-\delta}$ superlattices show the excellent thickness control obtained with this technique.

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[10] See, for example, *X-Ray Diffraction*, A. Guinier (Freeman, San Francisco, 1963), p. 121.
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